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CONTRACT NO. N00014-86-K-0772

TECHNICAL REPORT NO. 29

^{2}H NMR Studies of Oriented Fluid Phases

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Prepared for Publication

in

The Proceedings of
Macromolecules 1988 International Symposium
Kyoto, Japan, August 1988

October 19, 1988

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified	1b RESTRICTIVE MARKINGS None
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release, Distribution Unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 29	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION University of Connecticut 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research
6c ADDRESS (City, State, and ZIP Code) Storrs, CT 06268	7b ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217
8a NAME OF FUNDING/SPONSORING ORGANIZATION 8b OFFICE SYMBOL (If applicable) ONR/DARPA	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0772
8c ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)

"^{2}H NMR Studies of Oriented Fluid Phases" (Unclassified)

12 PERSONAL AUTHOR(S)
Edward T. Samulski

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Interim technical	FROM _____ TO 10/19/88	1988, 10, 19	9

16 SUPPLEMENTARY NOTATION
Prepared for publication in the proceedings of Macromolecules '88 International Symp., Kyoto, Japan, Aug. 1-6, 1988. (LCPRC Publication No. LCPRC88-20

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB GROUP	NMR Liquid Crystalline Polymers Polypeptide

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth J. Wynne	22b TELEPHONE (Include Area Code) (202) 696-4410 22c. OFFICE SYMBOL ONR

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
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^{2}H NMR Studies of Oriented Fluid Phases

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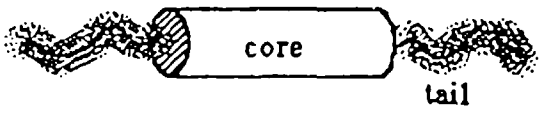
Abstract - Deuterium NMR observations are presented for two kinds of liquid crystals, thermotropic dimer mesogens and lyotropic polypeptide liquid crystals. In the former intramolecular averaging within the dimer spacer chain is suggestive of translational ordering within the nematic phase which is sensitive to the dimer's tenninal chain length. The averaging within the polypeptide sidechain appears to be dominated by intramolecular constraints— dihedral angle rotations.

Introduction

Two distinct topics are considered in this lecture: thermotropic dimer liquid crystals and lyotropic polypeptide liquid crystals. Both topics are considered in the context of deuterium NMR appraisals of inter- and intramolecular order. In the former melts, the focus is on the relationship between the ^{2}H NMR order derived from labelled dimers and that observed in polymer liquid crystals. New insights into the role of the terminal chains or tails in dimer liquid crystals emerge. In the lyotropic polypeptide liquid crystal we consider the sidechain secondary structure assumed by ethylene glycol derivatives of poly(glutamic acid) as a function of the sidechain length. The ^{2}H NMR observations are described with a rotational isomeric state approximate treatment of the sidechain internal degrees of freedom.

Thermotropic Dimer Liquid Crystals

There is continued interest in refining the molecular structural prerequisites for liquid crystallinity. In monomer or low molar mass liquid crystals (LCs) steric interactions are usually dominant. Consequently prolate LCs have the following general shape:



The flexible tails (hydrocarbon chains) on each end of the anisometric core merely facilitate the transformation from the solid state to the fluid phase at temperatures low enough for anisotopic excluded volume and attractive interactions to manifest themselves in the form of long range orientational order in the melt. That is, these terminal chains primarily lower the fusion temperature by establishing weak intermolecular interactions in the crystal. The aliphatic chains are generally segregated into strata in the crystal and interactions within strata are therefore limited to weak attractive dispersion forces. In the melt remnants of this stratification may remain and such translationally ordered fluids are called smectic LCs. Smectic phases are stabilized relative to less ordered LC phases when the length of the tail is increased. But this might be simply thought of as a microphase separation driven by the chemical difference between the core (usually aromatic) and the aliphatic tails. Herein we will limit consideration to nematic phases — uniaxial fluids in which the core axes are orientationally ordered relative to a director but the mesogen's center of masses are randomly distributed relative to the director (no longitudinal translational order other than short range packing as is characteristic of ordinary isotropic liquids). The latteral translational order is also short range (extending over a few molecular diameters) but may be somewhat higher than that found in ordinary liquids because of the average quasi-parallel arrangment of the major axes of the cores in the nematic.

In the nematic state it appears that the shape anisotropy of the mesogenic core determines whether a given organic molecule will exhibit a liquid crystalline melt. The terminal tails of the mesogen generally play an innocuous role in these ordered fluids. Herein we consider a series of dimer LCs constructed by linking two mesogenic cores together with a flexible aliphatic spacer chain:

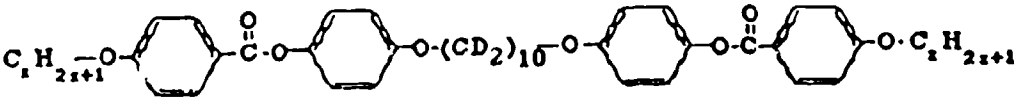
Explicitly, we examine the deuterium NMR quadrupolar splitting pattern exhibited by nematic phases of such dimers having a deuterium labelled spacer chain of constant length (ten methylene units) when the length of the aliphatic tails is varied. Our findings suggest that their may be a translational ordering role of the terminal tails in the nematic state which may have been overlooked in previous studies.

In its simplest form deuterium NMR provides a direct measure of the average orientation of a deuterium labelled C—H bond vector relative to the nematic director from the magnitude of the quadrupolar splitting:

$$\Delta\upsilon = \frac{2}{3} q S \qquad (1)$$

where $S = \langle P_2(\cos \theta)\rangle$ is the C—H order parameter and q is the quadrupolar coupling constant (q = 168 kHz for an aliphatic deuteron). The brackets < > signify an average over the anisotropic molecular motion in the liquid crystal. At the C—H bond level this motion includes internal isomerization of the spacer chain and anisotropic reorientation of the dimer itself. By merely observing the splittings themselves we obviate model-dependent efforts to deconvolute these two kinds of motion.

The labelled dimers have the following structural formula:



The spacer chain is deuterium labelled and two dimers were examined: x = 5 denoted 5.10.5 and x= 10 (10.10.10). Earlier Griffin and Samulski contrasted the ^2H NMR quadrupolar splitting pattern of 10.10.10 with that exhibited by the corresponding polymer LC (a linear alternating copolymer with the same mesogenic core linked into a chain with a ten-methylene spacer) and concluded from the appearance of the quadrupolar splitting patterns that the constraints on the spacer chains were distinctly different for the dimer and the polymer (ref. 1). The latter mesophase exhibited larger quadrupolar splittings and as one lowered the temperature of the polymer deep into the nematic phase the quadrupolar splittings at each site in the spacer became equivalent. The large values for S and the site-independent values of S in the spacer embedded in the polymer were attributed to severe intra-chain constraints stemming from the connectivity of successive cores and spacers in the polymer backbone (ref. 1). These conclusions should be modified in view of new findings on dimers reported here. In short, high molecular weight mesogens (extended connectivity) is not necessary for observing large values for S and the site-independent values of S in the spacer. Such behavior may be seen in dimers when the terminal chain of the dimer is one half of the length of the spacer chain.

Before examining the ^2H NMR of the neat dimers it is of interest to compare these dimers having defferent length terminal chains in dilute solution. In such a comparison the intrinsic intramolecular differences between the dimers and how these differences might influence spacer chain quadrupolar splittings can be appreciated in the absence of effects stemming from the intermolecular organization of the dimers in their respective melts. Figure 1 contrast the quadrupolar splittings exhibited by 5.10.5 and 10.10.10 as solutes (< 5 wt %) in a nematic solvent at the same reduced temperature, i.e., at the same degree of nematic mean field strength acting on each of the dimers. The complex intra- and extra-molecular motion of the solute dimers is biased in the nematic solvent and this shows up in the form of an incompletely averaded quadrupolar interaction at each labeled site in the spacer chain. However, despite the intrinsic structural differences between the two dimers (different terminal chain lengths), the quadrupolar splitting patterns of both dimers are identical within experimental uncertainties. This observation implies that the constraints that are operative in the nematic mean field of the solvent are effecting both spacer chains in exactly the same way independent of the structural differences between 10.10.10 and 5.10.5. That is, the terminal chain (length) does not influence the anisotropic motions (isomerization and molecular diffusion) affecting the averaging of the quadrupolar interactions within the spacer chains of these two different dimers. This would appear to validate the descriptor "innocuous" applied to the role of terminal chains in mesogens and corroborate the thinking on this subject inferred from a wide body of literature on simple mesogens having alkyl terminal chains.

It is clear from the distinct quadrupolar splittings apparent in the spectra in Figure 1 that the mode of averaging the C—H bond vectors differs at different sites in the spacer chain, but that the same behavior is observed in both dimers. This

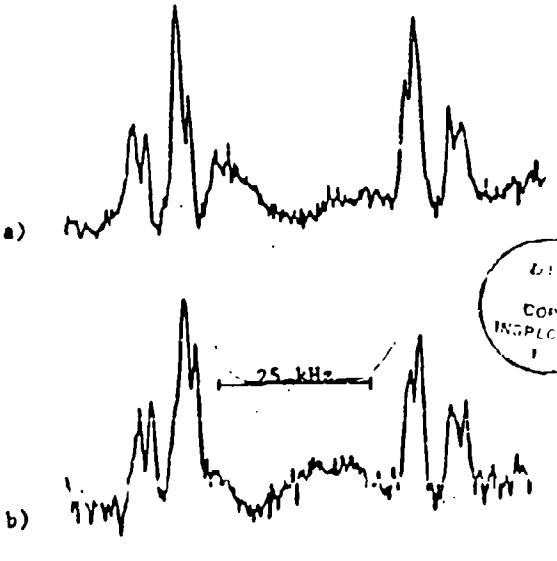


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Figure 1. Deuterium NMR spectra of dimers dissolved in a nematic solvent (>5% wt. dimer) at T_{red} = 0.985. a) 5.10.5 dimer; b) 10.10.10 dimer.

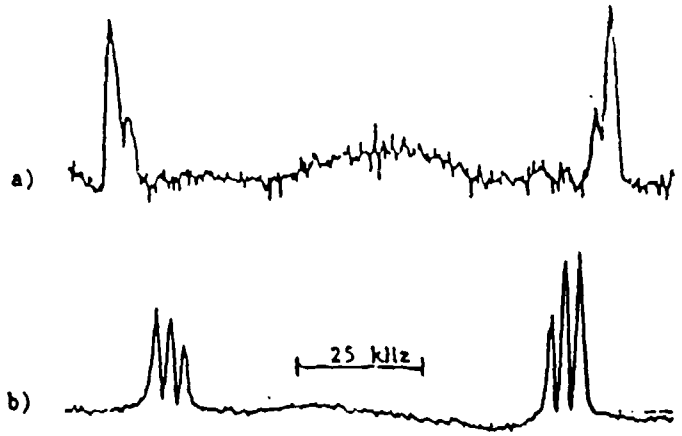


Figure 2. Deuterium NMR spectra of dimers in there respective neat nematic phases at the same reduced temperature T_{red} = 0.96. a) 5.10.5 dimer; b) 10.10.10 dimer.

simple result does not apply to the nematic phases of the neat dimers. Figure 2 shows the quadrupolar splitting patterns for the 10.10.10 and 5.10.5 at the same reduced temperature in their respective nematic phases. A cursory examination of the spectra indicates that 1) the orientational order is higher in the nemtaic phase of 5.10.5 than in the nematic phase formed by 10.10.10; 2) the constraints at different sites in the spacer chains are very different in the neat phases of the two dimers. In 10.10.10 (Figure 2a) three distinct splittings indicate three different categories of motional averaging among the spacer chain's methylene sites. (These sites could be unambiguously asigned by specific labeling experiments or approximate modeling schemes.) In 5.10.5 (Figure 2b) virtually all of the methylene units are averaged in the same way independent of the location of the methylene site in the spacer chain giving a single splitting — a superpostion of all of the (five possible) quadrupolar splittings. Interestingly, the ^2H NMR spectrum of 5.10.5 is strikingly similar to that of the polymer liquid crystal (ref. 1). This observation suggests that the quadrupolar splitting pattern of the polymer is not dominated by intramolecular constraints associated with the connectivity intrinsic to the long chain as previously suggested (ref. 1). Rather, the observed quadrupolar splitting patterns of the polymer and the dimers appear to be dictated by rather local intermolecular considerations.

It is intriguing that the 5.10.5 spacer should experience constraints so similar to those operative in the polymer mesophase. This finding prompts us to look for a supramolecular explanation of the implications of Figure 2. The similarity between the 5.10.5 dimer and the polymer suggests the presence of longitudial translational ordering in this dimer (formation of strings or chains of dimers). In the polymer nematic phase the local environment derives from close-packed, linear chains each comprised of a regular alternating core and spacer sequence along the logitudinal direction (parallel to the director). Is it possible to extend the idea of covalent longitudinal ordering in the polymer to rationalize in a simple way the large NMR difference between the 10.10.10 and 5.10.5 dimers?

Consider the idealized, (instantaneous) intermolecular arrangements of dimers imagined to be confined to translate along the director within parallel tubes (schematically illustrated in Figure 3). In Figure 3a and 3b, possible arrangements of 5.10.5 dimers are depicted that have enhanced, intermolecular core-core interactions (presumed to stabilize and promote orientational ordering) indicated by the shaded, interacting pairs of cores. Both exact lateral registration (Figure 3a) between a pair of 5.10.5 dimers and three-body combinations (Figure 3b) allow such idealized core-core interactions between both cores of a single dimer (lower dimer in each sketch). By contrast the three-body mode of interaction results in a partial interaction (involving only one core) in the 10.10.10 dimer (Figure 3c) because of the longitudinal incommensurability inherent in the 10.10.10 dimer's structure/length. In short, the additional length of the hydrocarbon tail in 10.10.10 relative to 5.10.5 dilutes core-core interactions in a rather specific manner. In the idealized nematic phase

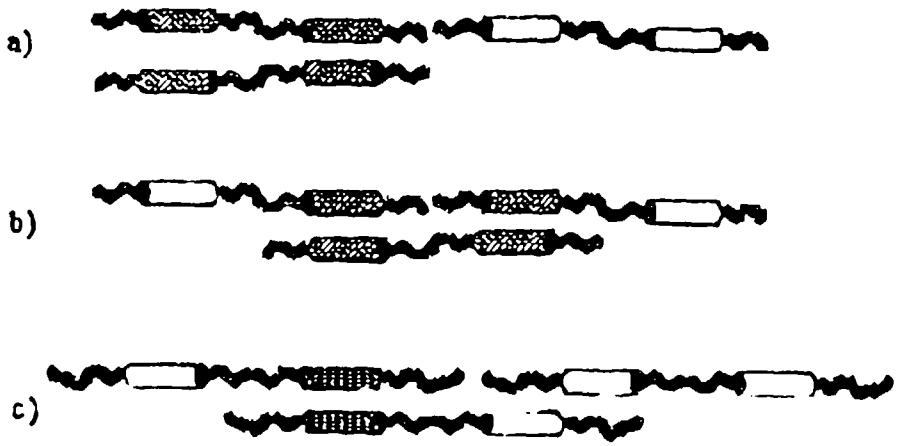
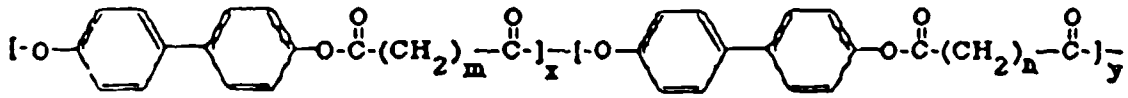


Figure 3. Idealized representations of intermolecular arrangments in the nematic phases of dimers: a) and b) 5.10.5 dimer configurations; c) 10.10.10 dimer configuration. The shaded mesogen cores enjoy perfect lateral registration.

comprised of the 5.10.5 dimer, one can visualize intermolecular translational order parallel to the director having a regular sequence (...core.10.core.10.core.10.core...), corresponding to the covalent longitudinal repeat of the covalent copolymer. In retrospect, the 10.10.10 dimer with the idealized alternating sequence (...core.10.core.20.core.10.core...) is not a good model of the polymer and these new ^2H NMR observations in dimers underscore the potential importance of terminal chains insofar as supramolecular, translational ordering obtains in dimer and in monomer nematic liquid crystals.

These findings and our supramolecular interpretation also has implications for polymer LCs themselves. Deliberately perturbing the regularity of a linear copolymer's sequence may have profound consequences for the phase type and its stability (temperature range). There is, in fact, evidence in the literature that moving from a commensurable copolymer (...core.spacer.core.spacer.core...) to an incommensurable one (...core.spacer.core.spacer '.core...) has dramatic effects on the mesophase stability. Watanabe and Krigbaum (ref. 2) examined (random) copolymers consisting of a mesogenic core and two different length spacers:



These copolymers (for 50:50 x:y copolymers of (even) spacers m = 10, 8, and 6 with spacer n = 12) formed smectic mesophases. A dramatically increasing mesophase temperature range is observed as the desparity between m and n is increased (ref. 2). For m = n/2, a monotropic nematic phase is observed above a wide, eutectic-like smectic phase. Clearly introducing longitudinal incommensurability into the primary structure of linear polymers has a profound effect, one that overshawdows the well-known even-odd effect in liquid crystals. It would appear that this phenomenon warrants further study and that it undoubtedly has a comparable analogy in the form of copolymer micro-sequence distribution in more conventional, linear, thermotropic polyesters — an analogy which could conceivably be exploited to produce more technologically viable thermotropic polymers.

Lyotropic Polypeptide Liquid Crystals

Mesophase formation in concentrated solutions of alpha-helical polypeptides has been known for some forty years. X-ray data (ref. 3) and more recent ^2H NMR (ref. 4,5) data show that the helix axis is aligned rather well with an order parameter in excess of 0.80. In the early magnetic resonance studies of these LCs, it was demonstrated that the solvent is also partially oriented as a result of a combination of specific solvation of the oriented helices and non-specific anisotropic diffusion among the array of parallel helices in these mesophases (ref. 6). ^2H NMR studies also demonstrated that the sidechain on the exterior of the polypeptide is partially oriented (ref. 7). In an effort to determine to what extent sidechain orientation is determined by non-specific interactions (similar to sovent orientation) versus intra-macromolecular constraints (covalent attachment to the aligned helical backbone), we prepared deuterium labelled derivatives of poly(L-glutamic acid) wherein the label at the sidechain terminus could be investigated as a function of the sidechain length. Esters with the following structure were labelled in the terminal methyl unit:

$$-(NHCO\underset{\underset{R}{|}}{CH})_x- \qquad R = -CH_2CH_2COO-(CH_2CH_2O)_n-CD_3$$

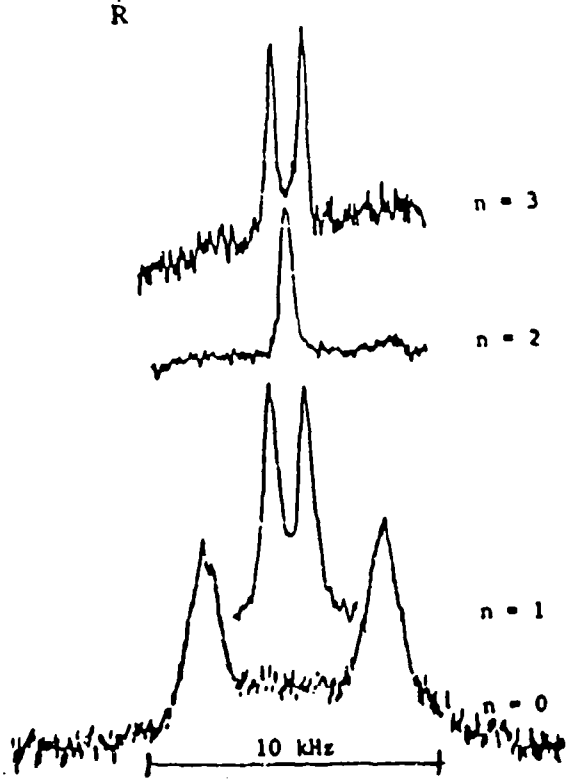


Figure 4. Deuterium NMR spectra of labelled methyl termini of ethylene glycol sidechains in esters of poly-L-glutamic acid (20% wt. in dichloromethane; 300K).

In the as pr[illegible]pitated (isotropic) polymers, solid state ^{2}H NMR shows progressive mobility of the sidechain terminus for the series [illegible] 1,2, and 3 (ref. 8). In the oriented liquid crystalline solutions (20 wt % polypeptide in dichloromethane), well resolved quadrupolar splittings are observed for this series (Figure 4; n = 0 corresponds to the methyl ester of glutamic acid). The magnitude of the observed quadrupolar splitting changes with increasing sidechain length and is independent of polymer concentration in the accessible mesophase range. The latter observation indicates that the anisotropic averaging of the sidechain is dominated by intra-sidechain considerations and that non-specific contributions (interhelix packing constaints) are neglegible. Hence it should be possible to correlate the observed sequence of splittings with the increasing number of internal degrees of freedom (dihedral angles) as the sidechain is lengthened.

If we examine ratios of quadrupolar splittings, i.e., relative to the n = 0 case, we find that this ratio is directly related to the bond correlation function $\langle P_2(\cos \phi_{1j})\rangle$ where the brackets indicate an average over all sidechain conformations and the angle 01j is the angle between the first O—CD_3 bond (n = 0) and the jth terminal O—CD_3 bond (n(j) = 1(4), 2(7) and 3(10)). The index of the bond j is illustrated in the schematic diagram in Figure 5. $\langle P_2(\cos \phi_{1j})\rangle$ can be calculated using the rotational isomeric state approximation and published values of the dihedral angle statistical weights. Figure 6 shows a comparison of calculated values of $\langle P_2(\cos \phi_{1j})\rangle$ with observed experimental ratios of the quadrupolar splitting. There is good semi-quantative agreement between calculation and experiment. The apparent absence of a splitting for n = 2 is predicted using conventional values for E_g (= -0.5 kcal/mol for the C—C bonds and +1.0 kcal/mol for the C—O bonds); all non-bonded interactions are included In the form of Lenard-Jones potentials for (united) atoms separated by four or more bonds in the sidechain. Quantitative agreement between experiment and calculation can be achieved by varying E_g values along the sidechain (ref. 8). Optimal values are within the experimental uncertainties of E_g (ref. 9), and tend to force the sidechain into a more extended all trans conformation. The necessity for using larger E_g-values to achieve quantitative agreement with experiment undoubtedly compensates for steric crowding among the close-packed sidechains on the periphery of the alpha-helix. More realistic multi-sidechain modeling with excluded volume interactions may very well yield more extended sidechain conformations (effectively, increased values of E_g).

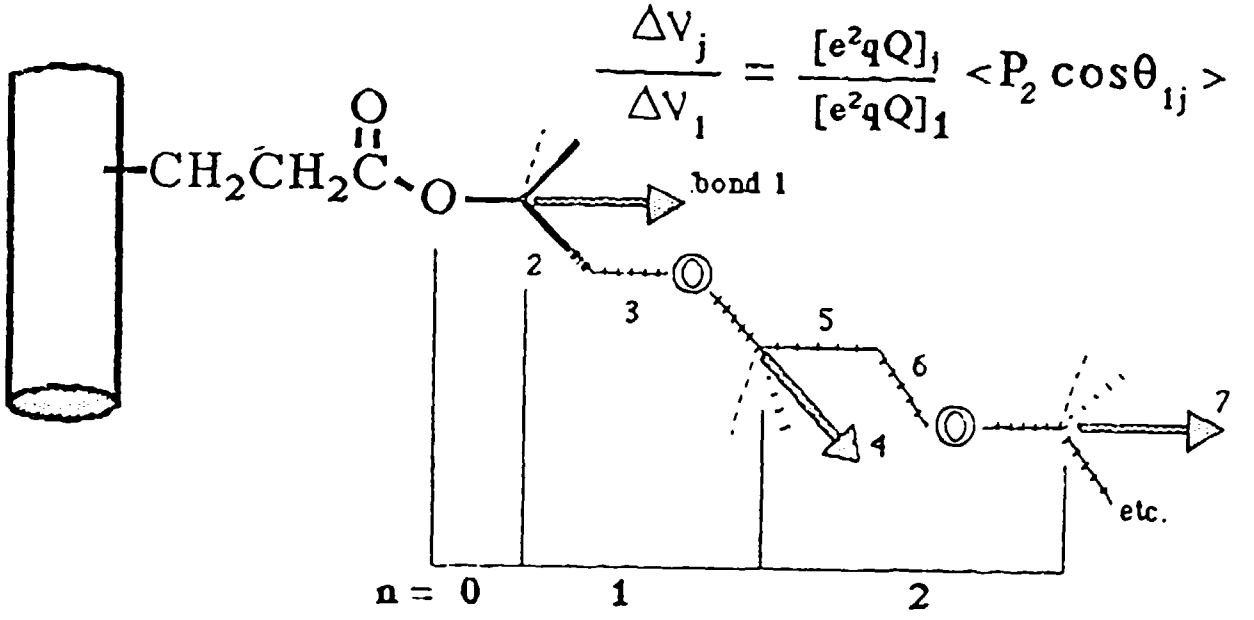


Figure 5. Schematic diagram and labeling of the polypeptide sidechain.

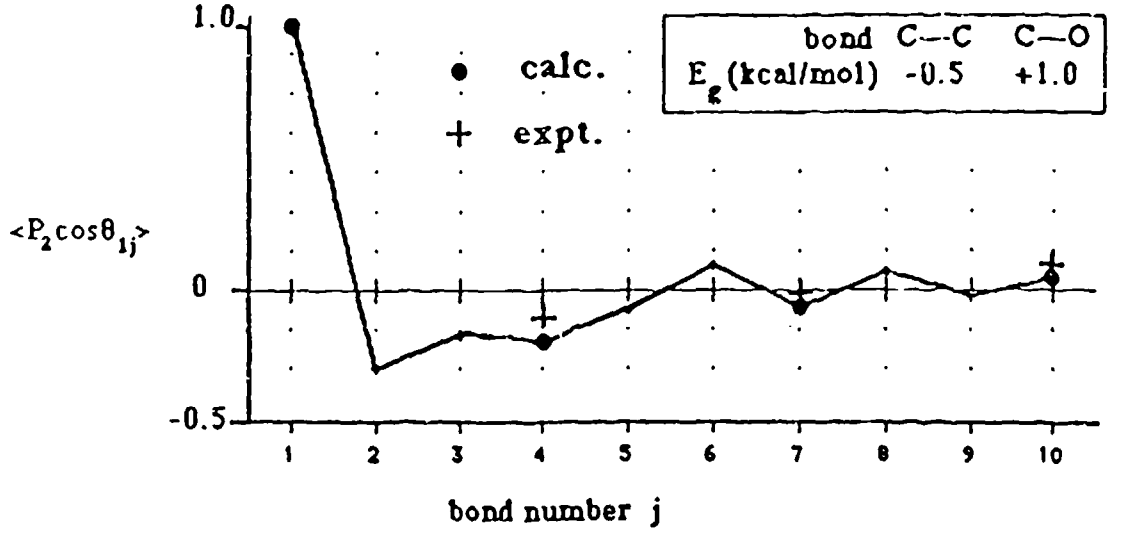


Figure 6. Calculated and observed bond correlation functions $\langle P_2(\cos \phi_{1j})\rangle$ versus sidechain length.

The detailed picture of sidechain secondary structure in these new polypeptides may be of value in elucidating the mechanism of ionic conduction when conventional polymers such as poly(ethylene oxide) are doped with ions (ref. 10). Preliminary sudies of ionic conductivity in these systems suggest ionic mobilities that are comparable to those in conventional polymeric electrolytes (ref. 8). This aspect of these new polypeptides take on additional consequences when (magnetically) oriented, uniaxial films are prepared by casting lyotropic liquid crystalline solutions. In fact, it may be possible to establish anisotropic ionic conductivity in these novel polymers.

Acknowledgment

I am indebted to A. C. Griffin for providing samples of the deuterium labelled dimers; the related NMR spectroscopy constitutes part of the Ph.D. thesis of M.D. Poliks (University of Connecticut, 1987). Y-W. Park prepared and investigated the new polypeptides (Ph.D. University of Connecticut, 1988). This research is supported by subcontract from the Liquid Crystalline Polymer Research Center, University of Connecticut (DARPA/ONR Contract No. N0014-86-K-0772)

References

1. A. C. Griffin and E. T. Samulski, J. Amer. Chem. Soc. 107, 2975-2976 (1985).
2. J. Watanabe and W. R. Krigbaum, Macromolecules, 17, 2288-2295 (1984).
3. N. S. Murthy, J. R. Knox and E. T. Samulski, J. Chem. Phys., 65, 4835-4839 (1976).
4 M. D. Poliks, Y-W. Park, and E. T. Samulski, Molec. Crys. & Liq. Cryst., 153, 321-346 (1987).
5. T. Yamazaki and A. Abe, Polym. J., 19, 777 (1987).
6. K. Czarniecka and E. T. Samulski, Molec. Crys. & Liq. Cryst., 63, 205-214 (1981).
7. E. T. Samulski, J. Physique, Paris, 40, C-3 471-474 (1979).
8. Y. W. Park and E. T. Samulski, in preparation.
9. A. Abe and K. Tasaki, Macromolecules, 19, 2647-2648 (1986).
10. J. I. Kroschwitz, Edt., Electrical and Electronic Properties of Polymers: A State-of-the-Art Compendium, John Wiley & Sons, New York (1988).

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